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Preparation and Characterization of Bis[2-(2-pyridyl)benzimidazole]iron(II) Complexes

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Bis[2-(2-pyridyl)benzimidazole]iron(II) complexes, $Fe(PBI)_2X_2$ ($X=Cl^-$, Br^-, NCS^-, N_3^-, and CN^-), were prepared and characterized on the basis of their infrared and Mössbauer spectra. In $Fe(PBI)_2(NCS)_2$, the NCS^- groups are N-bonded. The CN^- groups of $Fe(PBI)_2(CN)_2 2H_2O$ are in a *cis* position. Except for $Fe(PBI)_2(CN)_2 2H_2O$, the Mössbauer parameters are in the range characteristic of a Fe^{2+} ion in a high-spin form. On the other hand, the parameters of $Fe(PBI)_2(CN)_2 2H_2O$ are characteristic of an iron(II) ion in a low-spin form.

INTRODUCTION

Iron(II) octahedral complexes may exist in either one of two different electronic ground states, $^5T_2$ (high-spin $t_2^4e^2$) and $^1A_1$ (low-spin t_2^6). If $|\Delta-\pi|$ is smaller than 2000 cm^{-1}, where Δ represents a lignad-field splitting and π a mean pairing energy of *d* electrons, an equilibrium between the $^1A_1$ and $^5T_2$ states can be expected to occur[1]. Certain tris[2-(2-pyridyl)benzimidazole]iron(II) complexes exhibit anomalous magnetic behaviors indicative of the $^5T_2$-$^1A_1$ crossover.[2,3]

We have prepared bis[2-(2-pyridyl)benzimidazole]iron(II) complexes $Fe(PBI)_2X_2$ ($X=Cl^-$, Br^-, NCS^-, N_3^-, and CN^-) and characterized on the basis of their infrared and Mössbauer spectra to obtain further features of the iron(II) complexes of 2-(2-pyridyl)benzimidazole.

EXPERIMENTAL

2-(2-Pyridyl)benzimidazole was prepared by using the procedure described previously.[3]

Preparation of Complexes.

All the preparations were carried out in a nitrogen atmosphere using air-free water, acetone, and 3-methyl-1-butanol. All the complexes were dried *in vacuo* over silica gel at room temperature.

(a) Dichlorobis[2-(2-pyridyl)benzimidazole]iron(II) Monohydrate, $Fe(PBI)_2Cl_2H_2O$: 2-(2-Pyridyl)benzimidazole dissolved in acetone was added to a ferrous chloride solution prepared by mixing ferrous sulphate heptahydrate and barium chloride dihydrate solutions. When acetone was added to the filtered solution, reddish-brown crystals were precipitated. *Found:* C, 53.60; H, 3.67; N, 15.47%. Calcd for $C_{24}H_{20}N_6OCl_2Fe$: C, 53.86; H, 3.77; N, 15.71%.

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(b) Dibromobis[2-(2-pyridyl)benzimidazole]iron(II) Monohydrate, $Fe(BPI)_2Br_2H_2O$: This red complex was prepared as described in (a) by using barium bromide dihydrate instead of barium chloride dihydrate. *Found:* C, 46.43; H, 3.15; N, 13.49%. Calcd for $C_{24}H_{20}N_6OBr_2Fe$: C, 46.18; H, 3.23; N, 13.47%.

(c) Dithiocyanatobis[2-(2-pyridyl)benzimidazole]iron(II), $Fe(PBI)_2(NCS)_2$: 2-(2-Pyridyl)benzimidazole dissolved in the minimum of acetone was added to a ferrous chloride solution. A concentrated aqueous solution of NaSCN was added to the filtered dark-red solution and the mixture led alone for some time. The reddish-brown crystals thus precipitated were filtered, suspended in 3-methyl-1-butanol and then refluxed for 6 hr.

(d) Diazidobis[2-(2-pyridyl)benzimidazole]iron(II) Monohydrate, $Fe_2(PBI)_2(N_3)_2H_2O$: A concentrated aqueous solution of NaN_3 was added to a filtered solution of ferrous chloride and 2-(2-pyridyl)benzimidazole. After a while, the deep brown crystals were filtered.

(e) Dicyanobis[2-(2-pyridyl)benzimidazole]iron(II) Dihydrate, $Fe(PBI)_2(CN)_22H_2O$: A concentrated aqueous solution of NaCN was added to a filtered solution of ferrous chloride and 2-(2-pyridyl)benzimidazole, and the purplish red crystals were filtered and then refluxed for 6 hr in acetone. *Found:* C, 58.09; H, 3.52; N, 20.53; Fe, 10.55%. Calcd for $C_{26}H_{22}N_8O_2Fe$: C, 58.44; H, 4.15; N, 20.97; Fe, 10.45%.

While the values of elementary analysis of $Fe(PBI)_2(NCS)_2$ and $Fe(PBI)_2(N_3)_2H_2O$ coincided with the calculated ones respectively, the Mössbauer spectra of these complexes show that some of $Fe(PBI)_2Cl_2$ is mixed in these samples.

Infrared Spectra.

The infrared spectra were measured in Nujol mull with a Perkin-Elmer 521 spectrophotometer.

Mössbauer Effect Measurements.

The Mössbauer spectra were obtained with a scanning velocity spectrometer in the time mode. The radiation source was ^{57}Co diffused in a copper foil and kept at room temperature during all the measurements. The velocity scale was calibrated with metallic iron, and the velocity was determined to an accuracy of ± 0.06 mm/s.

RESULTS AND DISCUSSION

Infrared Spectra.

The infrared frequencies attributed to the vibrations of the X ligands in the $Fe(PBI)_2X_2$ complexes ($X=NCS^-$, CN^-, and N_3^-) are listed in Table I. The spectrum of $Fe(PBI)_2(CN)_22H_2O$ is shown in Fig. 1. Since the absorption bands due to 2-(2-pyridyl)benzimidazole of these complexes change little from $Fe(PBI)_2Cl_2H_2O$ and $Fe(PBI)_2Br_2H_2O$, it is easy to assign the bands due to the X ligands.

The thiocyanate group is a bifunctional ligand and the fundamental frequencies

Table I. Infrared Frequencies of Ligands X in $Fe(PBI)_2X_2$ Complexes (in cm^{-1})

Compound	Frequencies of band maxima	Assignment
$Fe(PBI)_2(NCS)_2$	2037 2045 2079	C-N stretching
$Fe(PBI)_2(CN)_2 2H_2O$	2050 2070	C-N stretching
$Fe(PBI)_2(N_3)_2H_2O$	2039 2060 2079	N-N stretching

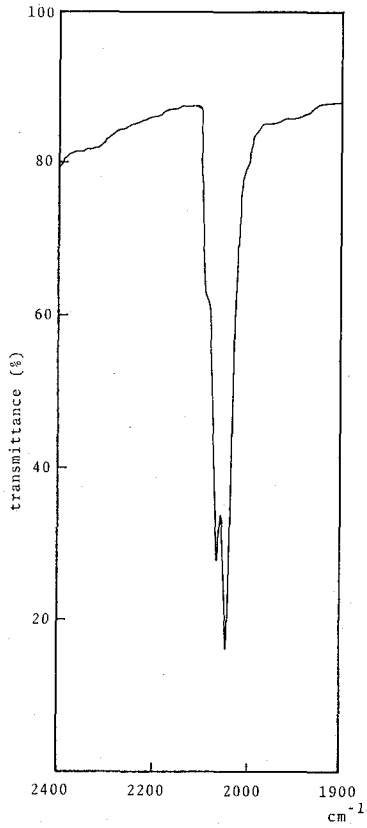

Fig. 1. Infrared spectrum of $Fe(PBI)_2(CN)_2 2H_2O$.

based on the C-N stretching vibration depend on whether this group is attached to the metal ion through N or through S. For M-NCS the range appears to be about 2040–2080 cm^{-1} and for M-SCN about 2080–2120 cm^{-1}.[4,5] In $Fe(PBI)_2(NCS)_2$, the band maxima are observed at 2037, 2045, and 2079 cm^{-1} being in the range characteristic of N-bonded thiocyanate.

Previous investigations have been concentrated on the infrared measurements of C-N frequencies of some mixed cyanide and aromatic diimine complexes of iron.[6,7] In the case of $Fe(phen)_2(CN)_2$ one could expected coupling to split the C-N stretching frequency into two stretching motions. The symmetric stretch would, however, be inactive in the *trans* complex (D_{2h}). A. A. Schilt reported that C-N stretching frequencies of the complex are 2075 and 2062 cm^{-1} in a *cis* form, and 2066 cm^{-1} in

a *trans* form.[8] In $Fe(PBI)_2(CN)_2 2H_2O$, the C-N stretching shows two peaks at 2070 and 2050 cm^{-1}. While asymmetric 2-(2-pyridyl)benzimidazole leads the complex into a lower symmetry, the C-N stretching mode would be rather sensitive to the position of the cyano ligands. Thus the splitting of the C-N stretching vibration suggests that the cyano groups are in a *cis* position.

Mössbauer Spectra.

The Mössbauer parameters are listed in Table II and the spectra are shown in Fig. 2. All the complexes were measured at *ca.* 110 K.

Table II. Mössbauer Parameters of $Fe(PBI)_2X_2$ Complexes

Compound	δ mm/s	ΔE_Q mm/s
$Fe(PBI)_2Cl_2H_2O$	1.08	2.63
$Fe(PBI)_2Br_2H_2O$	1.06	2.53
$Fe(PBI)_2(N_3)_2H_2O$	1.08 1.06	2.63 2.12
$Fe(PBI)_2(NCS)_2$	1.08 1.08	2.63 2.07
$Fe(PBI)_2(CN)_2 2H_2O$	0.31	0.74

110 K error = ±0.06 mm/s

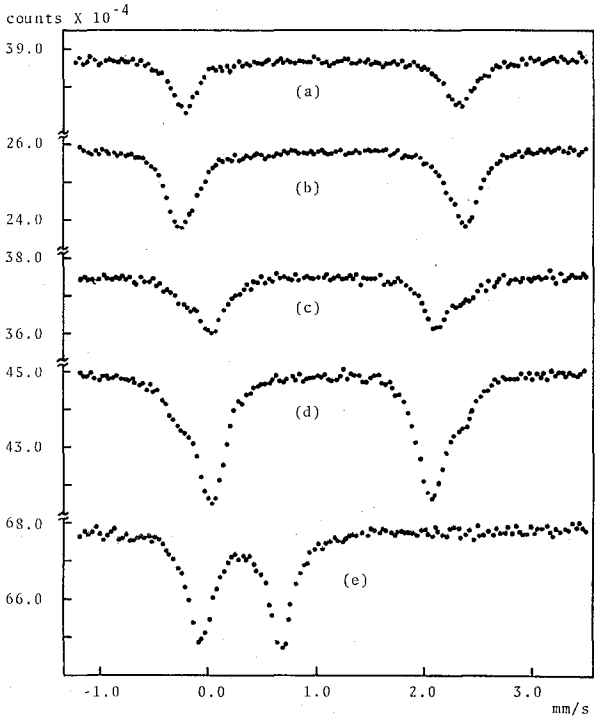

Fig. 2. Mössbauer spectra of $Fe(PBI)_2X_2$ complexes at *ca.* 110 K.
(a) $Fe(PBI)_2Br_2H_2O$ (b) $Fe(PBI)_2Cl_2H_2O$ (c) $Fe(PBI)_2(NCS)_2$
(d) $Fe(PBI)_2(N_3)_2H_2O$ (e) $Fe(PBI)_2(CN)_2 2H_2O$

The parameters of $Fe(PBI)_2X_2$ ($X=Cl^-$, Br^-, NCS^-, and N_3^-) are in the range characteristic of a Fe^{2+} ion in a high-spin form.[9] The spectra of $Fe(PBI)_2(NCS)_2$ and $Fe(PBI)_2(N_3)_2H_2O$ consist of two doublets. The outer pairs of both complexes center at 1.08 mm/s with a quadrupole splitting of 2.63 mm/s, whose parameters are consistent with the values of $Fe(PBI)_2Cl_2H_2O$. Since acetone was used in considerably large quantities to dissolve 2-(2-pyridyl)benzimidazole in the preparation, there is a possibility for $Fe(PBI)_2Cl_2$ to be coprecipitated. Thus we conclude that the outer peaks are attributed to $Fe(PBI)_2Cl_2$. On the other hand, the parameters of $Fe(PBI)_2(CN)_22H_2O$ are characteristic of an iron(II) ion in a low-spin form.

The octahedral complexes of FeA_4B_2 type may exist in either one of two different isomers, *cis* and *trans*. While some correlation between the quadrupole splitting and the geometry in high-spin complexes has not been reported, previous investigations has been intently performed on such a relationship in low-spin compounds.[10~14] The calculations according to a point charge model predict that the quadrupole splitting of the *trans*-compounds should be twice that of the *cis*-isomer in magnitude. The relationship has been observed in several series of *cis-trans*-isomers of iron complexes.[11~13] But in $Fe(phen)_2(CN)_2$, the quadrupole splitting of the *cis*-complex is 0.58 mm/s and that of the *trans*-isomer 0.60 mm/s at room temperature.[11] The quadrupole splitting of $Fe(PBI)_2(CN)_22H_2O$ is 0.74 mm/s in *ca.* 110 K, which is slightly larger than those of *cis*- and *trans*-$Fe(phen)_2(CN)_2$. Therefore, Mössbauer effect would not be as yet an effective tool to determine the structure of mixed cyanide and α-diimine complexes of iron(II).

The bis[2-(2-pyridyl)benzimidazole]iron(II) complexes, $Fe(PBI)_2X_2$, may be classified into three groups on the basis of their magnetic properties: (i) if $X=Cl^-$, Br^-, NCS^-, and N_3^-, $Fe(PBI)_2X_2$ is a high-spin compound ($^5T_2$ ground state); (ii) $[Fe(PBI)_3]^{2+}$ complexes in which X_2=2-(2-pyridyl)benzimidazole exhibit a spin equilibrium between $^1A_1$ and $^5T_2$ states,[2,3] (iii) $Fe(PBI)_2(CN)_22H_2O$ is a diamagnetic complex ($^1A_1$ ground state). The magnetic property of octahedral iron (II) complexes depends on the balance of the crystal-field splitting and the Racah's parameters in magnitude. In the spectrochemical series, the order of the ligands related to this study is $Br^- < Cl^- < N_3^- < -NCS^- <$ dipy~phen $< CN^-$. The classification of the other α-diimine iron (II) complexes on the basis of their magnetic properties, also, shows that there is a similar relationship between the spin state of their complexes and the spectrochemical series of the ligands.[15~21] The tris(1,10-phenanthroline)iron(II) and tris(2,2'-bipyridyl)iron(II) complexes are diamagnetic, and $Fe(phen)_2(NCS)_2$ and $Fe(bipy)_2(NCS)_2$ have an anomalous magnetic properties due to a $^1A_1$ and $^5T_2$ crossover.[18,19] Such a change in the spin state for ligand to ligand indicates that 2-(2-pyridyl)benzimidazole gives rise to a weaker ligand-field than do 1,10-phenanthroline and 2,2'-bipyridyl in iron(II) complexes.

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